

# Quantum Relaxation of Ensembles of Nanomagnets

N. V. Prokof'ev<sup>1</sup> and P. C. E. Stamp<sup>2,3</sup>

<sup>1</sup> *Russian Research Center "Kurchatov Institute", Moscow 123182, Russia*

<sup>2</sup> *Department of Physics and Astronomy, and Canadian Institute for Advanced Research, University of British Columbia, 6224 Agricultural Rd., Vancouver B.C., Canada V6T 1Z1*

<sup>3</sup> *Institut Laue-Langevin, Ave. des Martyrs, Grenoble 38042, France*

*Recent theory and experiment in crystals of molecular magnets suggest that fundamental tests of the decoherence mechanisms of macroscopic quantum phenomena may be feasible in these systems (which are almost ideal quantum spin glasses). We review the results, and suggest new experiments.*

The attempt to push quantum effects to mesoscopic or macroscopic scales has led, in magnetic systems, to various interesting discoveries. Theoretical work on domain wall tunneling<sup>1,2,3</sup> led to experiments claiming to see tunneling of single domain walls.<sup>4</sup> Early theory on tunneling of large spins<sup>5,6</sup> stimulated experiments on resonant tunneling in crystals of magnetic macromolecules,<sup>7,8,9,10,11,12</sup> and on "macroscopic quantum coherence"<sup>13</sup> in giant ferritin molecules.

There is a theoretical complication - the environmental "spin bath" of nuclear and paramagnetic spins should destructively interfere with any tunneling.<sup>14,15,16,17</sup> In fact, except in ferritin, all experiments see *incoherent* tunneling relaxation at low T. A detailed theory of such relaxation,<sup>18,19,20,21</sup> applied to ensembles of tunneling nanomagnets, makes several "universal" predictions for the relaxation characteristics, some of which have now been verified.<sup>22,23</sup> Here we discuss the recent developments, and suggest future experiments designed to bring out the fundamental role of nuclear spins in quantum decoherence at low  $T$ .

## 1. Kinetics of Quantum Relaxation

Our problem is simple but general. Consider an array (ordered or otherwise) of identical 2-level systems (which here represent large spins;  $S \gg 1$ , below the crossover temperature  $T_c$  of confinement to their 2 lowest levels). Their Hamiltonian is<sup>21</sup>

$$H = \frac{1}{2} \sum_{i \neq j} V_{ij}^d \hat{\tau}_z^{(i)} \hat{\tau}_z^{(j)} + \sum_j \Delta \hat{\tau}_x^{(j)} + \sum_{jk} V_N(\hat{\tau}_z^{(j)}, \{\vec{I}_k\}) + H_{NN}, \quad (1)$$

where  $V_{ij}^d$  describes dipolar interactions between nanomagnets  $\{i, j\}$ ,  $\Delta$  is the tunneling amplitude between states  $\alpha = \pm$ ,  $V_N$  couples nanomagnets to nuclear spins  $\{\vec{I}_k\}$ , and  $H_{NN}$  describes the *intrinsic* nuclear spin dynamics. Note that without  $V_N$ , Eq. (1) describes the “quantum spin glass” problem;<sup>24</sup> the effect of  $V_N$  is to couple this to an environment.

The entire system is described by normalised probability distributions for single molecules, pairs of molecules, etc.; thus  $P_\alpha(\xi, \vec{r}; t)$  is the probability that a molecule at position  $\vec{r}$  has polarisation  $\alpha = \pm$  and bias  $\xi = \epsilon_+ - \epsilon_-$  between states  $|\pm\rangle \equiv |\pm S\rangle$ . The bias  $\xi$  at  $\vec{r} = \vec{r}_i$  sums the nuclear bias (of typical energy scale  $E_0$ ), the dipolar bias  $\sum_j V_{ij}^d \tau_z^{(j)}$  (typical energy scale  $E_D$ ), and any bias from external fields. This 1-particle distribution  $P_{(1)}$  is connected to higher distributions  $P_{(2)}, P_{(3)}$ , etc., via a BBGKY- style hierarchy of kinetic equations.<sup>21</sup> Since the only part of the environment with any dynamics at low T and low H (ie., able to mediate irreversible incoherent tunneling) is the nuclear bath, the kinetic equation for  $P_{(1)}$  is governed by a nuclear-mediated transition rate  $\tau_N^{-1}$ , calculated in.<sup>18</sup> When the number of nuclear spins co-flipping with the molecular spin is small,

$$\tau_N^{-1}(\xi) \sim \tau_0^{-1} e^{-|\xi|/\xi_o}, \quad (2)$$

where  $\xi_o$  parametrises the range of fluctuations in  $\xi$ , and  $\tau_0^{-1} \sim \Delta^2/\xi_o$ ; typically  $\Delta \ll \xi_o \ll E_0, E_D$ .

Several unambiguous predictions<sup>21</sup> flow from the kinetic equation. Over a wide time range ( $E_D/\xi_0 > t/\tau_0 > \xi_0/E_D$ ) the magnetisation should relax from saturation according to a *universal square-root law*, i.e.,  $M(t) = M_0[1 - (t/\tau_Q)^{1/2}]$ . For ellipsoidal samples  $\tau_Q \rightarrow \tau_Q^{ell} = (E_D\tau_0/\xi_0)f(c)$  (where  $f(c)$  is an analytic function of the ellipsoid shape); for other shapes  $\tau_Q \sim \tau_0^{ell}/\xi_0 N_\uparrow(0)$ , where  $N_\uparrow(0) = \int d^3r P_\uparrow(\xi = 0, \vec{r}, t = 0)$  is the initial “up” distribution at zero bias. Since  $\tau_Q^{ell} \sim E_D/\Delta^2$ , we have  $\tau_Q \sim E_D^2/\Delta^2\xi_0$  for a generic shape (since  $N_\uparrow(0) \sim O(1/E_D)$ ). In Figure 1 we see why the square root prediction is valid independently of the details of the hyperfine couplings, the sample shape, or the ratio  $E_0/E_D$ ; it arises from the “Lorentzian hole”, eaten in the initial  $N_\uparrow(\xi)$  by the decay, coming from the long-range

## Quantum Relaxation of Ensembles of Nanomagnets

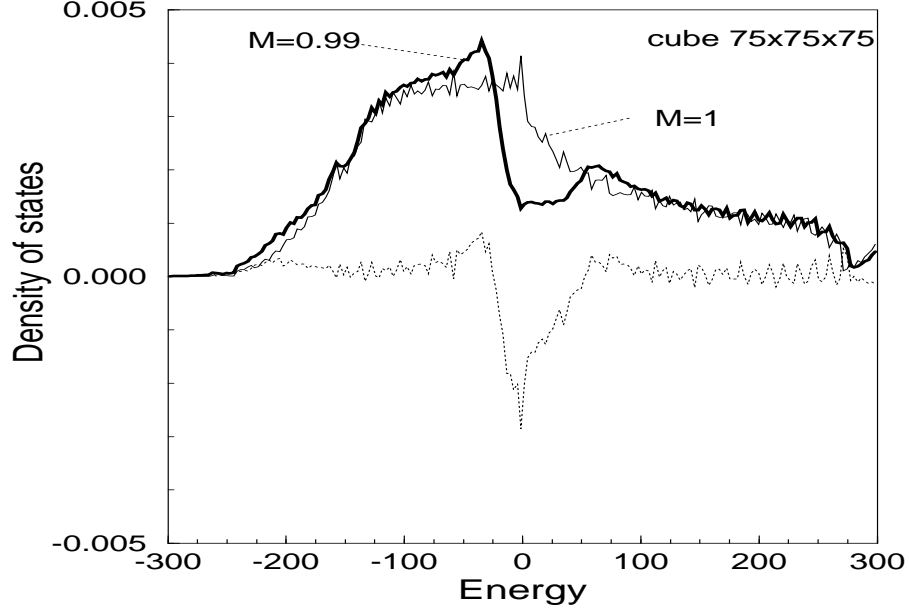


Fig. 1.

dipolar interactions.<sup>21</sup> Fig. 1 shows a Monte Carlo simulation for a cube of size  $(75)^3$  sites, and depicts  $N_{\uparrow}(\xi)$  when  $t = 0$  (so  $M = M_0$ ), when  $M/M_0$  has relaxed to 0.99; and the difference between the two. In a weak external field, we must replace  $N_{\uparrow}(0)$  in the expression for  $\tau_Q^{-1}$  by  $N_{\uparrow}(\xi = g\mu_B SH)$ ; thus a field scan will find that  $\tau_Q^{-1} \propto N_{\uparrow}(\xi = g\mu_B SH)$ , ie.,  $\tau_Q^{-1}(H)$  directly measures  $N_{\uparrow}(\xi)$ . Since  $N_{\uparrow}(\xi)$  can be calculated numerically (knowing  $E_0, E_D$ , and the sample shape), this is a testable prediction.

## 2. Universality and Crossovers

How "universal" is the square root law? One potential problem, given that the ligand groups in such large molecules can be unstable, is rogue fast-relaxing "impurity" molecules. Suppose the impurity concentration is  $\delta_0 \ll 1$ . Defining  $M_A(t) = (1 - \delta_0) - x(t)$ , and  $M_B(t) = \delta_0 - y(t)$ , for the bulk and impurity magnetisations, normalising  $M_0 = 1$ , and assuming a ratio  $\Lambda \gg 1$  between impurity and bulk relaxation rates, one gets a short-time behaviour

$$y(t) = \delta_0 [1 - \exp(-\Lambda x(t)/(1 + \delta_0))] , \quad (3)$$

$$t/\tau_Q^A = x^2(t) + 2\delta_0 \left[ x(t) + \frac{1 + \delta_0}{\Lambda} \left( \exp\left(-\Lambda \frac{x(t)}{1 + \delta_0}\right) - 1 \right) \right] . \quad (4)$$

One easily verifies that for arbitrary  $\Lambda\delta_0$ , any appreciable impurity contribution to  $dM/dt$  destroys square-root relaxation (conversely, square-root relaxation only appears if the impurity contribution is negligible).

The square root behaviour must also break down in the crossovers to long-time relaxation, and to thermal activation. After  $\sim 10 - 15\%$  of the sample has relaxed, the Lorentzian hole will distort because of intermolecular correlations. These are not because of multi-flip processes (which have rate  $\sim \Delta^4/\xi_0^2 E_D$ , and so are rare), but because factorisability of  $P^{(2)}$  fails. However at long times other universal results emerge. *First*, if hyperfine spread in  $N_\uparrow(\xi)$  is strong (ie., when  $E_0 > E_D$ ), then at times  $> T_1(T)$ , the  $T_1$  nuclear relaxation will sweep  $\xi(t)$  at any molecule over most of the range  $\Delta\xi$  of  $N(\xi)$ ; one then gets<sup>18</sup>  $M(t) \sim e^{-t/T_1(T)}$ , for  $t \gg T_1$ . For weak hyperfine coupling ( $E_0 \ll E_D$ ), intermolecular correlations give a complicated quantum spin-glass problem, with no "sweeping" mechanism to wipe out these correlations. *Second*, if we thermally recycle the sample, depolarising at high  $T$  until  $M(t)/M_0 \ll 1$ , the remaining relaxation will be exponential, at a rate<sup>21</sup> (with  $\kappa \sim 1$ ):

$$\tau_{long}^{-1} \sim \frac{2\xi_0}{\tau_0 E_D [1 + \kappa \ln(E_D/\pi\xi_0)]}, \quad (5)$$

The quantum-thermal crossover is more subtle. The *spin gap* in the system is  $\Delta\omega = (E_S - E_{-(S-1)})$ , between the lowest levels  $|\pm S\rangle$  and the next 2 levels  $|\pm(S-1)\rangle$ , and we expect that roughly  $kT_c \sim \Delta\omega/2\pi$  (in fact  $\Delta\omega \sim 11.6K$  ( $5.1K$ ) for Mn-12 (Fe-8) respectively, whereas experimentally  $kT_c \sim 2K$  ( $0.4K$ ). As noted above, if  $T \ll T_c$ , everything but the nuclear subsystem is frozen (dipolar flip-flop processes to levels  $|\pm(S-1)\rangle$  occur with frequency  $\sim \Omega_{dip} e^{-\Delta\omega/kT}$ , where the coupling  $\Omega_{dip} \sim 10^6 - 10^8 Hz$  in these systems; at the lowest temperatures ( $70mK$ ) used in the Fe-8 experiments,<sup>12</sup> the activation exponent was  $\sim e^{-70!!}$ ). In this case we expect square root relaxation; and  $\tau_Q$  will only depend on temperature to the extent that  $T_2$  does (ie., very little). However as one approaches  $T_c$ , molecular flip-flops are more frequent. The square root prediction is not affected- but  $\tau_Q$  can develop a thermally-activated component, because (a) now dipolar field fluctuations can also bring molecules to resonance, and (b) by exciting nuclear  $T_1$  transitions, they sweep the nuclear bias (this mechanism will only be important for strong hyperfine interactions). A detailed theory of this is quite complicated.<sup>25</sup>

Finally, in the very low- $T$  limit 2 things will happen; the nuclear spins will polarise in the hyperfine field, for temperatures below the hyperfine coupling  $\omega$ , and the nuclear  $T_2$  fluctuations will freeze out; and glass theory then predicts that a "dipolar gap" will open up in  $N_\alpha(\xi)$  if  $M \ll M_0$ .

## Quantum Relaxation of Ensembles of Nanomagnets

### 3. Experiments

Some of the predictions (such as the square root law in the quantum regime) have recently been found, in experiments on Fe-8 and Mn-12 single crystals.<sup>22,23</sup> However there is still no *direct* proof for the controlling role of nuclear spins in the quantum dynamics of nanomagnets; the observed  $\sqrt{t/\tau_Q}$  relaxation clearly shows the role of dipole interactions, but the evidence for the nuclear role is indirect. How can it be seen directly?

One obvious way is to do AC absorption experiments over a frequency range encompassing both  $\Delta$  and  $\xi_o$ . In Mn-12 and Fe-8,  $\Delta$  is perhaps  $10^{-10} - 10^{-8}K$ , some 8-10 orders of magnitude smaller than  $E_D$  or  $E_0$  (which is why it is so astonishing that one sees very low  $T$  relaxation at all); we expect  $\xi_o \sim 10^{-5}K$ . This test is discussed by Rose and Stamp.<sup>26</sup> A much more intriguing possibility would be available if NMR experimentalists could find resonance lines for some of the spin-5/2 Mn nuclei in Mn-12 (the zero-field hyperfine coupling is probably  $\sim 600$  MHz (450 MHz) on the spin-2 (3/2) Mn electronic sites respectively). At this point a "David and Goliath" experiment becomes possible; one "tickles" the nuclear spins at the resonance frequency, in order to control the relaxation of the giant magnetic molecules (eg. retarding the relaxation by changing  $\xi_o$ ). Another, probably more difficult experiment would "freeze out" the nuclear dynamics by cooling to  $kT \ll \omega_o$  (ie, well below  $30mK$  for Mn-12). The problem here is that of cooling the nuclei, since most of the heat transfer will involve the same  $T_2$  fluctuations that we want to freeze out! However there is a fundamental interest to doing this, since according to the theory these nuclear fluctuations are the last barrier to truly macroscopic coherent (MQC) behaviour in low- $T$  systems (note that recent work<sup>27</sup> indicates that nuclear and paramagnetic spins will make it very hard to see MQC even in *superconductors*; spin baths tend to be far more damaging to MQC than oscillator baths<sup>28</sup>). This, as well as the resulting "Quantum Spin Glass" behaviour in the unpolarised limit, means that the low- $T$  limit promises much to the intrepid experimentalist!

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# **N.V. Prokof'ev and P.C.E. Stamp**

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28. Another way to block the tunneling dynamics of even very small magnets is by making them *conducting*. Theory<sup>18</sup> indicates they should "quantum localise" by the usual orthogonality catastrophe, once  $\xi, kT < \Omega_0$  (switching on again very suddenly when  $kT$  or  $\xi \sim \Omega_0$ ). This prediction may have technological implications for future memory storage elements.